Comparison of ultrafiltration and dissolved air flotation efficiencies in industrial units during the papermaking process

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SUMMARY

The efficiency of an ultrafiltration unit has been studied and compared with a dissolved air flotation system to get water with a suited quality to be reused in the process. The study was done at a paper mill producing light weight coated paper and newsprint paper from 100% recovered paper. Efficiency was analysed by removal of turbidity, cationic demand, total and dissolved chemical oxygen demand, hardness, sulphates and microstickies. Moreover, the performance of the ultrafiltration unit and the membranes were studied deeply, analysing its variability during the filtration process.

As expected, the ultrafiltration gave higher removal efficiencies than the dissolved air flotation cell in parameters like turbidity, cationic demand, dissolved chemical oxygen demand and microstickies. The greatest difference in performance between the units concerned cationic demand and dissolved chemical oxygen demand. Ultrafiltration was influenced by the operating time, decreasing the removal efficiency of the dissolved fraction by 75% and of the colloidal fraction by 30% after 312 of running. Membrane autopsy, carried out to identify the cause of poor membrane performance, showed that the active layer was degraded due to the effect of suspended solids.

Keyboards: ultrafiltration, dissolved air flotation, anionic trash, dissolved and colloidal material, closure of water circuits

1. INTRODUCTION

There exist a worldwide trend in paper industries to reduce freshwater consumption for environmental and economical reasons (water stress, freshwater savings and reduction of effluent treatment and disposal costs) *(1,2)*. In modern paper mills, freshwater consumption can vary between 2 and 20 m^3 of water per tonne of paper produced, depending on the type of manufactured paper and on the age of the mill *(3)*. However, as the mills close their water systems, a considerable accumulation of contaminants exists, which can affect both the product quality and the efficiency of papermaking operations due to, e.g., deposit formation *(4,5)*. This situation is worse in recycling paper mills *(6-9)*.

Dissolved air flotation (DAF) is considered a traditional treatment to remove suspended solids (fines, fillers, or residual ink) effectively (80 to 98%) due to their colloidal nature.

Dissolved and colloidal matter (DCM) higher than 0.2 µm can be also removed from the water if suitable chemicals are added before the clarification unit. However, DCM smaller than 0.2 µm, normally remains within the process water, being necessary the use of advanced internal water treatments *(10-16)*. Various techniques have been developed to remove these contaminants from process waters. The best-known strategies include: membrane filtration, biological treatment under anaerobic or aerobic conditions, enzymatic treatments, use of oxidizing agents and multiple-effect evaporation. Each technology presents a different efficiency removal for each contaminant. Therefore, the idea is to find a technology with the minimum cost that reduces contaminants to a level that can be tolerated within the paper mill, without affecting product quality nor paper machine runnability *(17,18)*.

Membrane-based processes are physical unit operations and, therefore, present inherent advantages over the chemical and biological processes that are commonly used in wastewater treatment. Ultrafiltration (UF) and reverse osmosis (RO) systems are taking advantage as polishing treatment schemes to remove undesirable components, minimizing water consumption and reducing the concentration of contaminants. The high quality of the permeate allows its reuse within the papermaking process (e.g. paper machine showers), reducing freshwater intake. However, the main drawback of membrane systems is their sensibility to be fouled by suspended solids and, particularly, by DCM, or by precipitating salts, leading, at the end, to a permeate flux decline or to obtain a permeate stream of worse quality *(19-24)*.

In this paper, the efficiency of an industrial UF unit has been studied in detail and its performance has been compared with a DAF unit. The study was based on traditional analysis: consistency, ash content, turbidity, cationic demand (CD), conductivity, total and dissolved chemical oxygen demand (TCOD and DCOD), hardness, sulphates and microstickies analyses of process waters from different paper productions. The variability of the UF process on the efficiency of this unit and the behaviour of the membranes were also studied.

2. DESCRIPTION OF THE TREATMENT UNITS

Water samples were taken from a recycled paper mill using 100% recovered paper as raw material. This paper mill produces light weight coated paper (LWC) and newsprint paper (NP). Figure 1 shows a general flowsheet of the paper mill water loop where the DAF and UF units are integrated.

2.1 Ultrafiltration unit

The UF unit is placed in the machine circuit to treat the clear filtrate coming from the disc filter. This filtrate is screened through 0.2 mm and storaged in the feeding tank before entering the unit. The permeate will be used in the machine showers to clean the forming wire and rolls. For this application the water has to be of very high quality to avoid the clogging of shower holes and to keep the wires as clean as possible to optimize the drainage and the forming of paper sheet.

The UF unit (CR1010-100, METSO Paper, Finland) consists of a serial of cells or cassettes which are assembled one on top of the other. The membranes sheets, made of regenerated cellulose, are installed on both sides of each cell. Between each cassette there is a rotor, which rotation causes a high turbulence and a cross-flow across the membranes, keeping the solids and trash in constant movement, reducing the effect of fouling. The cell has three channels, one for the feed, which comes into the unit from the bottom; another for the concentrate, collected on the top; and the permeate, which is taken out at the bottom of the unit. Filtration phenomenon is achieved by maintaining 0.9 bar of transmembrane pressure (TMP).

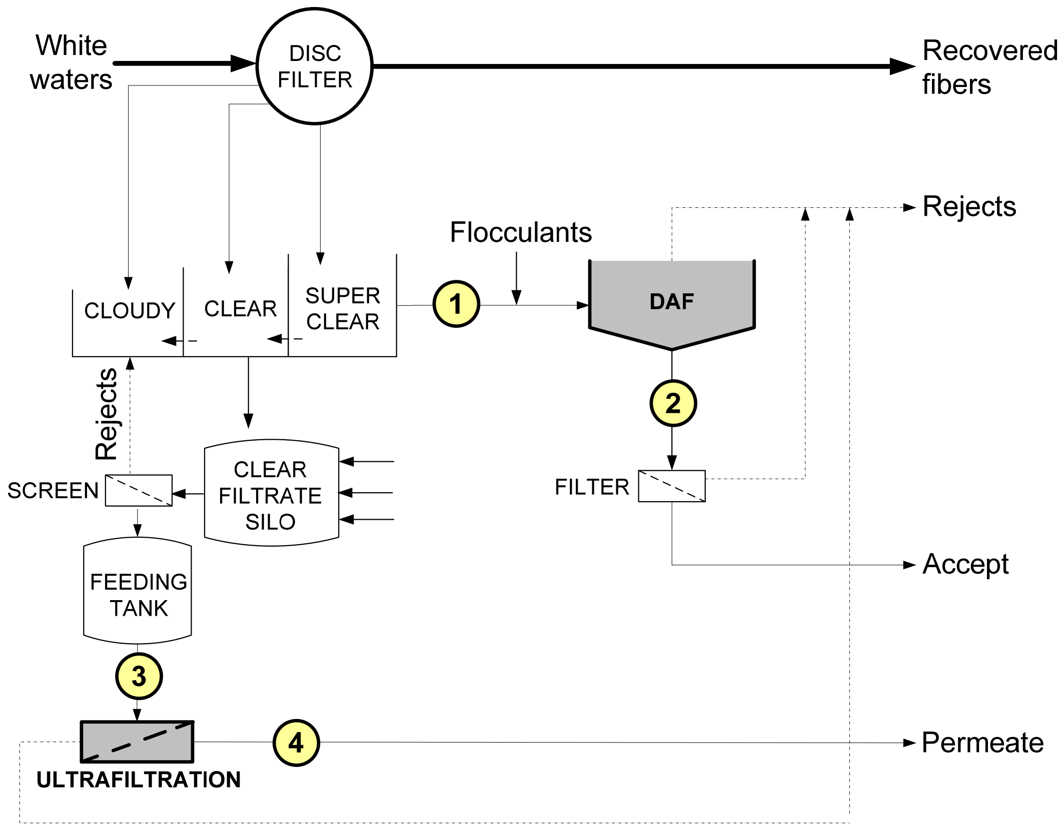


Fig. 1. Simplified flow-sheet of the paper mill water loop with the location of the sampling points.

To keep a constant permeate flow, the UF is cleaned chemically when its filtration capacity decreases 20 to 30% from the previous wash. Besides, although the filtration capacity does not decrease the mentioned percentages, maintenance cleanings are needed: a weekly cleaning with alkali and a monthly cleaning with an acid solution. Washing is started by pre-rinsing the unit with warm water; after this, the detergent solution is pumped to the UF and is kept in circulation for some time. After the stated time, the solution is kept inside the unit for a soaking period. Finally, the pump and the rotors start running again and the cleaning solution is flushed from the filter by clean warm water. After washing, the UF is ready for filtering.

2.2 Dissolved air flotation unit

The DAF unit ("KROFTA" SUPRACELL, Krofta Engineering Limited, India) is also placed in the machine circuit, in parallel with the UF, but its objective is to treat a fraction of the super-clear filtrate after the addition of 3 to 5 mg/L of a cationic polyacrylamide of medium charge density and ultra-high molecular weight. The water clarified in the DAF is used for pulp dilutions along the deinking process and at the flotation deinking cells showers to break the foam. Therefore, its quality is not so critical.

3. METHODS

As shown in Figure 1, the samplings points selected for the study of the DAF and UF units were the feed streams (1 and 3, respectively) and the accept or permeate streams (2 and 4, respectively). A total of five samplings were carried out, collecting the samples in different days and production conditions (Table 1). Both paper qualities were produced under conventional alkaline chemistry during pulping: NaOH (0.6-0.8%), H_2O_2 (0.9-1.1%), Na_2SiO_3 (0.3-0.4%) and soap (0.1-0.2%).

Table 1. Sampling conditions.

Trial	Conditions	Production	Unit	
1	312 hours running since start-up	LWC	DAF	UF
2	120 hours running since start-up	LWC	DAF	UF
3	120 hours running since start-up	LWC	-	UF
4	120 hours running since start-up	NP	DAF	UF

The samples were separated by size fractions before their chemical characterization, as shown in Figure 2. Water samples were filtered in a Büchner funnel with a paper filter of 7 µm (MN 640W, from Macherey-Nagel GmbH & Co) to obtain the colloidal fraction, which was filtered with a syringe filter of 0.45 µm (Millex, from Millipore) to obtain the dissolved fraction. All the parameters were measured twice. Consistency and ash were measured by a gravimetric method, filtering the water through the mentioned paper filter and drying it at 105 ºC for 1 hour. The filter, with the dried solids retained on it, was then dried at 525 ºC to obtain the ash content. Turbidity was measured with a LP 2000-11 nephelometer supplied by Hanna Instruments, according to ISO 7027:2001. Cationic demand was measured by colloidal titration of the samples with 0.001 N poly-diallyldimethylammonium chloride (PDADMAC). The end-point was detected with a PCD 03 particle charge detector (Mütek Analytic GmbH) used in combination with an automatic titrator, model Compact I (Crison Instruments, S.A). The COD was determined with Merck Chemicals Kit (1.14691.0001) using an Aquamate-spectrophotometer (AQA 091801), and a PF-11 Filterphotometer (Macherey-Nagel GmbH & Co) equipment was used to measure sulphates (Test 0-86) and hardness (Test 0-43). Sulphates content is a critical parameter for the paper mill where this study was done because all effluents sent to the Madrid sewerage network can not exceed the level of 1000 mg/L to avoid the corrosion of concrete pipes due to microbial sulfur metabolism *(25)*. During the manufacture of both paper grades, NP and LWC, sulfuric acid was added to the pulp to control pH in the paper machine. This sulfuric acid remains in the process water until it finally appears in the effluent as sulphates.

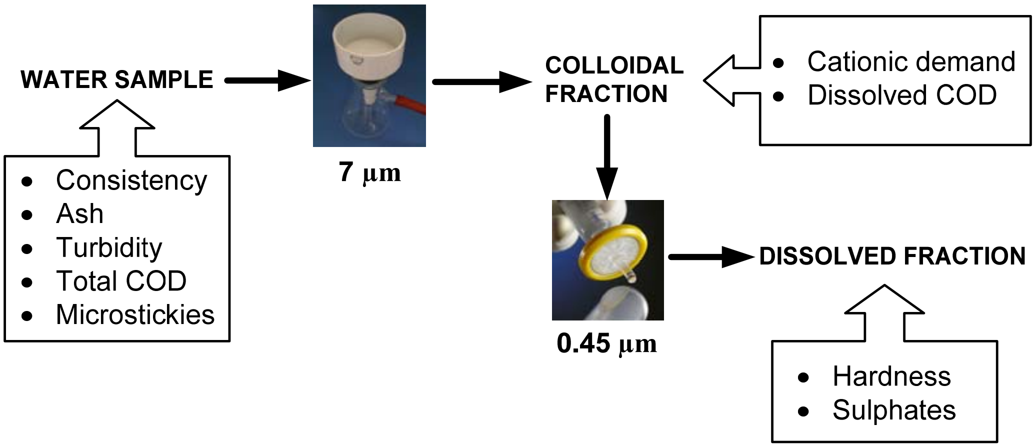


Fig. 2. Parameters measured in different fractions of the sample.

Microstickies were obtained using the deposition tester developed by the University Complutense of Madrid (UCM) and quantified by image analysis (Figure 3). The deposition tester consists of a vertical cylindrical rotor assembly with open ends, collector plates (films) lined with 0.05 mm thick stainless steel films, and an axial flow propeller. The propeller steers the liquid through the rotor assembly which directs the liquid toward the internal collector films which collect deposits by an impact mechanism. Simultaneously, the liquid passes the external plate which collects the deposits by a transference, or dynamic-fluid (flow) mechanism. The tests were carried out three times, using 1800 mL of sample. The stainless steel collectors are subsequently removed and dried before scanning with a commercial computer flatbed scanner (HP Scanjet 6100C) at 600 dpi. The resulting scanned images are analyzed using the image analysis system "Deposit Evaluation Software 1.2" developed also by the UCM Research Group *(26, 27)*. In this paper, the microstickies results are expressed as mm^2/L.

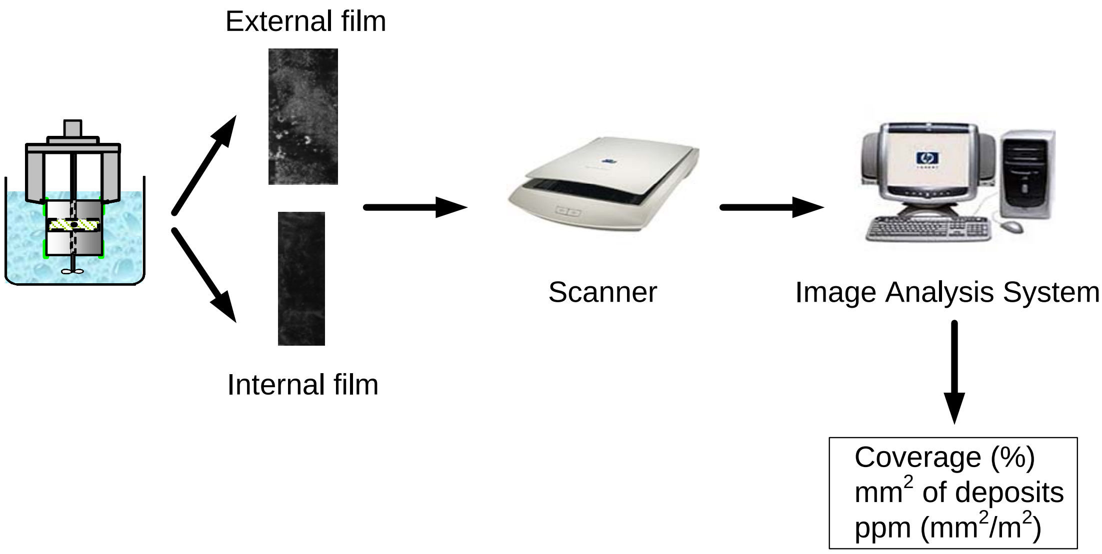


Fig. 3. Procedure followed to analyse microstickies.

An autopsy of the used UF membranes was carried out at the end of the trials to identify the cause of poor membrane performance. Mercury porosimetry technique (Micromeritics Autopore IV equipment) was used to determine membrane pore size distribution, and scanning electron microscopy (Philips XL30 microscope) was used to see the structure of the membrane layer.

4. RESULTS AND DISCUSSION

4.1 Effect of water chemical composition on the efficiency of DAF and UF units

The first objective was to compare the efficiencies of both units at similar operational conditions (120 h running since start-up) in both mill environments (LWC and NP), corresponding to trials 2 and 4 from Table 1.

The main parameters of the inlet and the outlet streams from each unit are shown in Table 2. All the parameters were measured twice (variability lower 5%), but microstickies, which were measured three times (variability lower 10%), and the values presented in Table 2 are the average value of all the measurements. Figure 4 represents the removal efficiencies achieved for each contaminant. The removal efficiencies are calculated using Equation [1].

$$R\,(\%) = \frac{X_f - X_o}{X_f} \cdot 100 \qquad [1]$$

Where, R represents the removal efficiency (%); X_f is the measured parameter in the feeding stream; and, X_0 is the measured parameter in the accepted or permeated stream.

Waters obtained during NP production have higher suspended solids and inorganic compounds. However, the colloidal fraction, represented by CD, DCOD and microstickies are higher in LWC production. These results were also observed by Miranda et al. in 2009 (4). The raw material used to produce NP and LWC papers had an approximate newsprint/magazine ratio of 1.3 and 0.9, respectively. As the proportion of magazines fed to produce LWC paper is higher, there is a higher proportion of coating binders being released into the process waters during pulping than in NP production *(28)*. The higher value of hardness in NP production could be a consequence of the lower pH of pulping in NP (7.5 to 7.6) than in LWC production (7.7 to 7.8), enhancing the dissolution of calcium carbonate *(4)*. Although total solubility of $CaCO_3$ is achieved below pH≈4.5, its solubility increases around 50 mg/L by changes on pH of only 0.5 units below pH=8.0 *(29)*. That is why minimal variations on pH produce important changes on hardness measurements.

Table 2. Water characterization depending on the type of paper production.

		DAF		UF	
	Production	**Feed (1)**	**Accept (2)**	**Feed (3)**	**Permeate (4)**
Consistency	*LWC*	0.04	0.003	0.04	0.001

(%)	*NP*	0.08	0.005	0.04	0.001
Ash (mg/L)	*LWC*	111	7	196	2
	NP	257	25	280	6
Turbidity (NTU)	*LWC*	739	62	634	5
	NP	2140	48	1720	1
CD (μeq/L)	*LWC*	370	368	247	50
	NP	154	158	155	141
TCOD (mg/L)	*LWC*	1155	781	657	277
	NP	1625	634	1298	484
DCOD (mg/L)	*LWC*	712	710	628	266
	NP	572	605	616	484
Hardness (mg/L)	*LWC*	151	157	131	74
	NP	201	194	217	200
Sulphates (mg/L)	*LWC*	198	198	386	203
	NP	343	341	346	348
Microstickies (mm^2/L)	*LWC*	459	115	1311	145
	NP	216	126	855	93

Normally, the solid content should decrease sequentially within the cloudy, clear and super-clear filtrates. Mäkinen et al. (2003) determined that during NP production the cloudy filtrate should normally contain 230 to 390 mg/L of solids, the clear filtrate approximately 80 to 135 mg/L and the super-clear 34 to 61 mg/L; while in LWC manufacturing the solids content is usually a bit higher: 250-400 mg/L, 85-145 mg/L and 38-65 mg/L, respectively. These values were presented for white waters with 0.8% of consistency (in the current study white water consistencies vary from 0.73% after 120h up to 0.95% after 312h), and the intervals are function of the speed of the disc filter (from 0.5 to 1.5 rpm). The higher values of consistency, ash and turbidity in the super-clear stream obtained in our trial (Table 2), besides of obtaining consistency values higher in NP production than in LWC, reveals that the disc filter was damaged and needed to be repaired. The higher value of TCOD in the super-clear stream is associated with the consistency, the higher the consistency, the higher the TCOD, as more fines and fibres are being oxidized during the analysis.

Figure 4 shows that the UF gave higher removal efficiencies than the DAF unit for parameters such as consistency, ash, turbidity, CD, DCOD and microstickies in both production environments. For NP production**,** removal efficiencies in TCOD were similar in both units; however, in LWC manufacturing better results were obtained after the UF. Solids removal efficiencies in DAF cells are normally better with increased solids in the feed stream. The greatest difference in performance between the units concerned CD and DCOD, which were not affected at all by the DAF operation, but decreased around 10% (NP), 80% (LWC) and 20% (NP), 60% (LWC), respectively, through the UF unit. According to Brun and Carré *(31)*, the removal efficiency of colloidal substances in DAF cells, measured in terms of CD, can vary between 10 and 40%, but dissolved and colloidal matter of inorganic and biological nature is hardly affected. This could mean that the filtrates obtained in the disk filter are mainly formed by these last substances. Reaching high percentages of CD and DCOD removal is an important aspect to prevent deposits promoted by stickies.

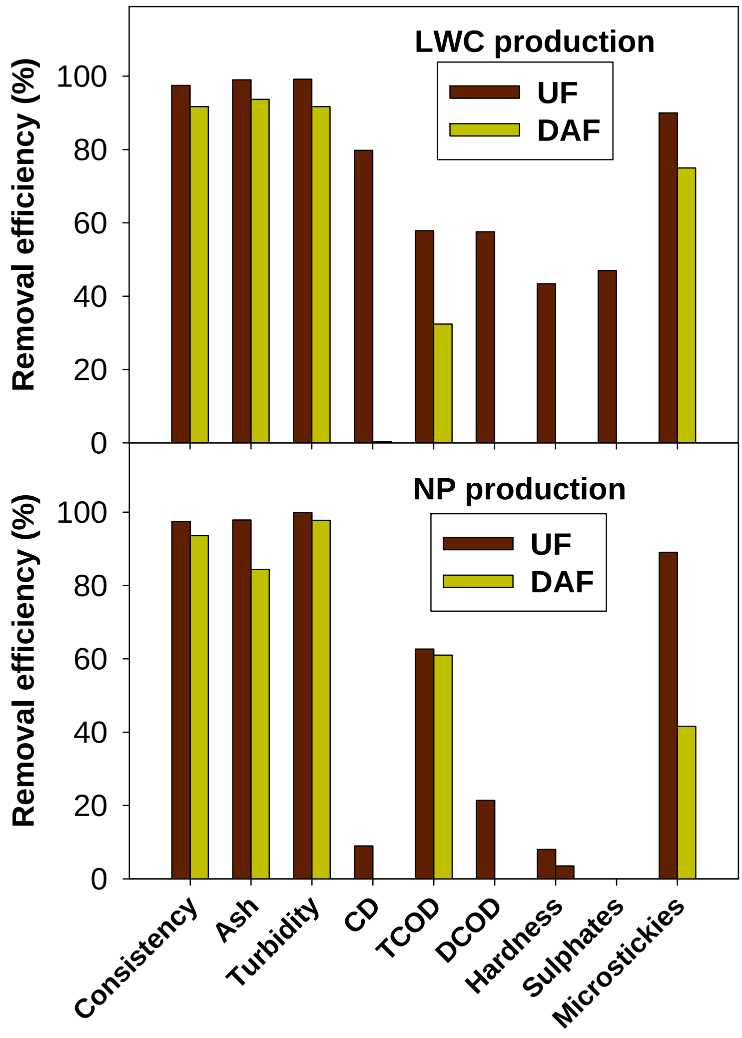


Fig. 4. Removal efficiencies in DAF and UF units depending on paper production.

4.2 Effect of water quality on the efficiency of DAF and UF units

The second objective of this study was to compare the efficiencies of both units after different operation times (120 and 312 h of operation since the start-up of the paper mill) during LWC production, corresponding to trials 1 and 2 in Table 1. Table 3 shows both the water chemical characterization at the inlet and outlet of both units, and the percentage increase of each contaminant at the longer operation time (from 120 up to 312 h). The accumulation in time of each contaminant is calculated using the Equation [2].

$$Accumulation\ (\%) = \frac{X_{f_{312}} - X_{f_{120}}}{X_{f_{120}}} \cdot 100 \qquad [2]$$

Where $X_{f_{312}}$ represents the measured parameter in the feed stream after 312h operation; and $X_{f_{120}}$ means the measured parameter in the feed stream after 120h operation.

Table 3. Water characterization in DAF and UF units depending on running time during LWC production.

		DAF			UF		
	Running time	**Feed (1)**	**Accumulation (%)**	**Accept (2)**	**Feed (3)**	**Accumulation (%)**	**Permeate (4)**
Consistency (%)	*120 h*	0.036	106	0.003	0.041	34	0.001
	312 h	0.074		0.004	0.055		0.001
Ash (mg/L)	*120 h*	111	74	7	196	38	2
	312 h	193		21	271		6
Turbidity (NTU)	*120 h*	739	-15	62	634	56	5
	312 h	627		116	987		2
CD (µeq/L)	*120 h*	370	107	368	247	206	50
	312 h	766		764	757		288
TCOD (mg/L)	*120 h*	1155	70	781	657	167	277
	312 h	1969		1408	1755		1218
DCOD (mg/L)	*120 h*	712	88	710	628	128	266
	312 h	1339		1312	1434		1231
Hardness (mg/L)	*120 h*	151	-17	157	131	4	74
	312 h	126		137	136		132
Sulphates (mg/L)	*120 h*	198	368	198	386	168	203
	312 h	927		957	1035		965
Microstickies (mm^2/L)	*120 h*	459	14	115	1311	41	145
	312 h	521		190	1846		186

As expected, the quality of the inlet stream got worse with operation time. Furthermore, considerable variability in the process is observed in some cases. For example, parameters such as CD and sulphates at both, DAF and UF inlet streams, increase over 100%.

Figure 5 shows the removal efficiencies of both units. After 312 h of operation, DAF lost 5 to 15% of its efficiency in ash, turbidity, TCOD and microstickies removal, while CD, DCOD, hardness and sulphates were not removed at all. To the contrary, the operation time did not affect consistency, ash and turbidity removal efficiencies in the UF, but it affected in an important manner DCOD, hardness and sulphates removal efficiencies, which were reduced more than 70%.

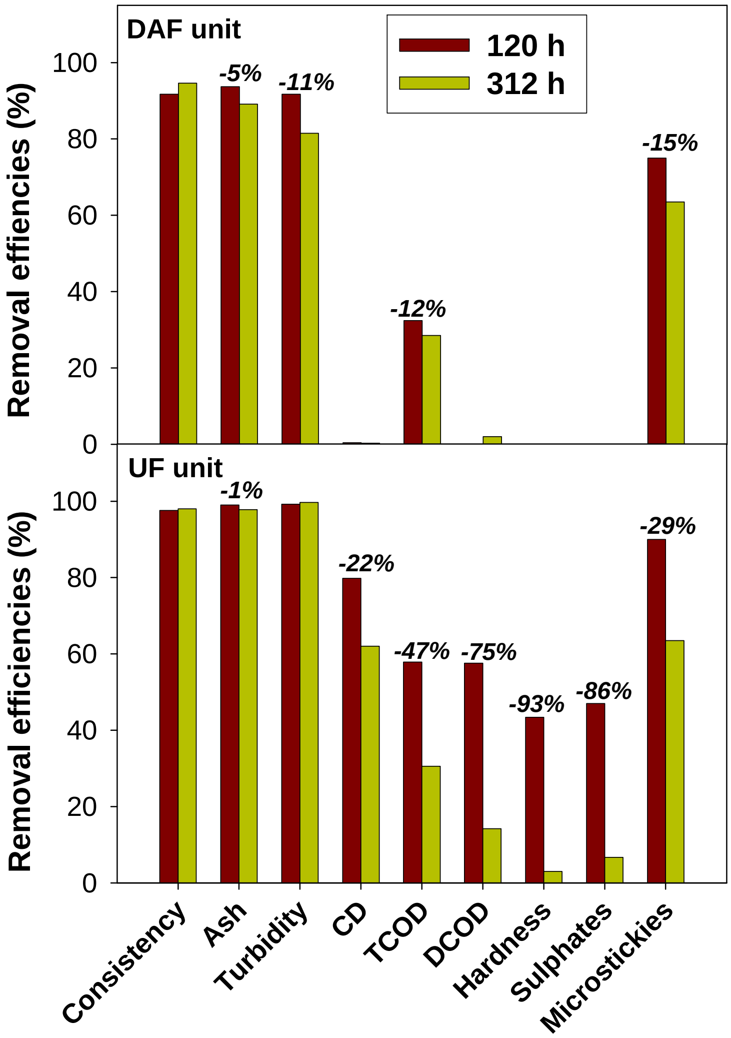


Fig. 5. Removal efficiencies for DAF and UF at different operation times.

4.3 Study of the UF unit

4.3.1 Variability of the UF process

The variability of the UF process was assessed by the performance of two samplings carried out at the same conditions: LWC paper production and 120 h of operation after the starting-up (trials 2 and 3 in Table 1). Variability of water quality (RSD) was determined by Equation [3] *(32)*. Table 4 shows the average parameter of water characterization at the inlet and outlet streams, the percentage of water quality variability and the removal efficiency of each parameter.

$$\pm RSD(\%) = \frac{X_i - \overline{X}}{\overline{X}} \cdot 100 \qquad [3]$$

Where, *RSD* is the variability of water quality (%); X_i represents the measured value; and $\overline{X}$ represents the mean value of the two measurements (three in microstickies) of the parameter being considered.

Table 4. Variabilities of water quality and UF removal efficiencies.

	Average feed (3)	**Average permeate (4)**	**Average efficiency (%)**
Consistency (%)	0.039±0.001 (4% RSD)	0.0015±0.0005 (33% RSD)	96.2±1.5 (2% RSD)
Ash (mg/L)	178±18 (10% RSD)	3.5±1.5 (43% RSD)	98.0±1 (1% RSD)
Turbidity (NTU)	398±236 (60% RSD)	4±1.0 (25% RSD)	98.8±0.4 (0.5% RSD)
CD (µeq/L)	296±49 (17% RSD)	91.5±41.5 (45% RSD)	70.7±9.1 (13% RSD)
TCOD (mg/L)	793±136 (17% RSD)	525±248 (47% RSD)	37.4±20.5 (55% RSD)
DCOD (mg/L)	775±147 (19% RSD)	472.5±206.5 (44% RSD)	42.0±15.6 (37% RSD)
Hardness (mg/L)	146±15 (10% RSD)	107±33 (31% RSD)	28.0±15.4 (55% RSD)
Sulphates (mg/L)	229±157 (69% RSD)	135.5±67.5 (50% RSD)	25.7±21.3 (83% RSD)
Microstickies (mm^2/L)	762±549 (72% RSD)	121±24 (20% RSD)	72.5±17.5 (24% RSD)

Most of the parameters (consistency, ash, CD, TCOD, DCOD and hardness) of the feed showed 15% of variability. However, turbidity, sulphates and microstickies resulted in variabilities higher than 60%. These variations depend on the specific quality of the raw materials within the same recycled paper grade. However the variability of the permeate parameters is higher than 20% in all cases.

There is not a correlation between the variability of the feed or the permeate parameters and of the UF efficiency. For example, although turbidity varied 60% respecting its mean value, the efficiency of the UF reflected a variability of 0.5% from the mean. However, hardness variability was 10% and the removal efficiency varied 55%. Therefore, independently of the consistency, ash and turbidity values in the feed stream, the UF achieves removal efficiencies higher than 50%.

It is known that membranes are built on different layers with a varied pore size distribution *(33)*. In fact, as a result of the mercury porosimetry, the structure of the UF membranes analyzed in this study is based on three differentiate layers: (a) the support layer with an average pore size of 3 µm; (b) an intermediate layer with an average pore size of 0.4 µm; and (3) the active layer with pore sizes between 0.1 and 0.005 µm.

The active layer does not have a fixed cut-off limit for the matter present in water, and this explain why large colloidal and particulate material, represented by consistency and turbidity, is better removed and with a lower variability, than small colloidal and dissolved particles.

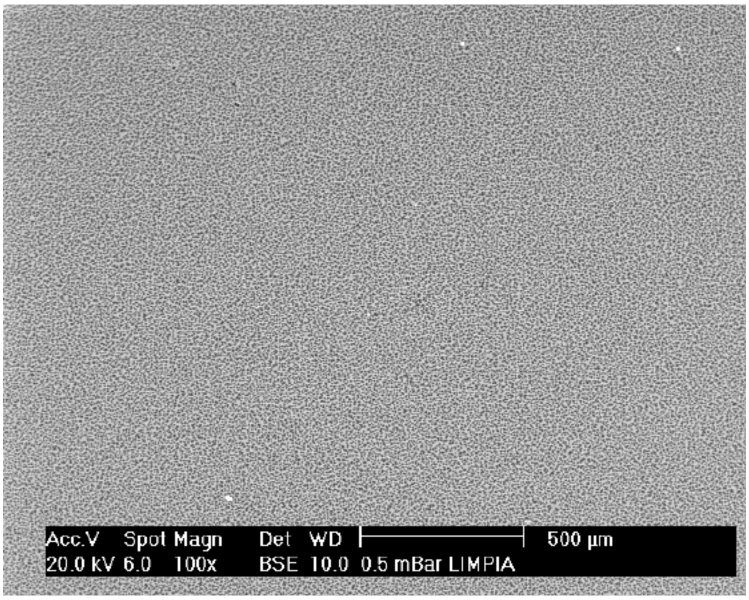
4.3.2 Autopsy of the UF membranes

After developing all the previous study, two important questions come out: why removal efficiencies in DCM are lower during NP production? and why the operation time affected UF removal efficiencies at short times?

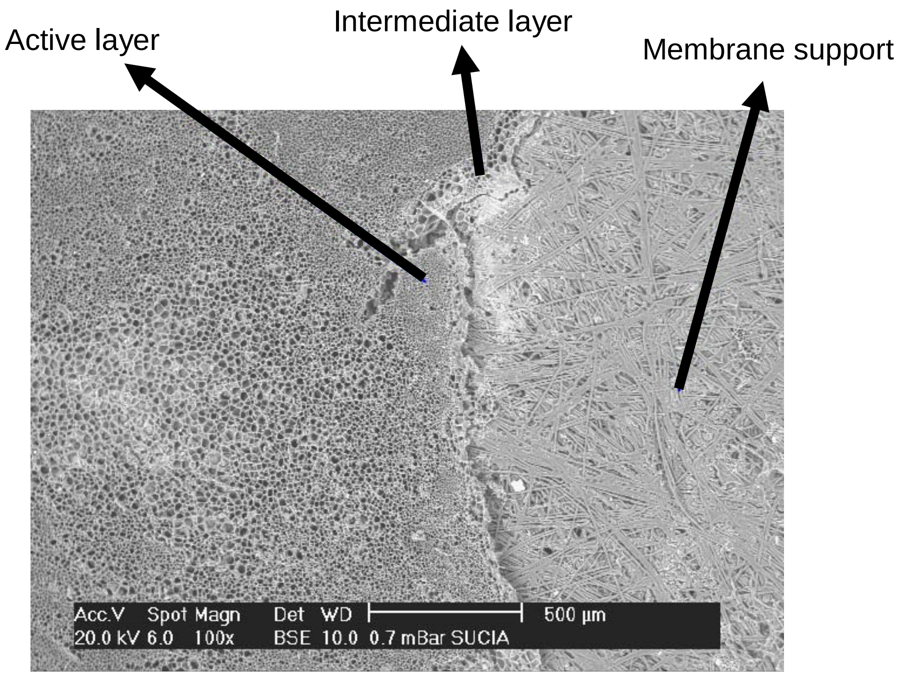
An autopsy of the used membranes was done after finishing the trials. Figure 6 shows two microphotographs of the membrane surface before (Figure 6a) and after (Figure 6b) using it.

The three different membrane layers mentioned in section 4.3.1 are distinguished in Figure 6b; where it can be concluded that the active layer of the membrane was completely degraded in the areas where the support is visible. This degradation is a consequence of the abrasive effect of the suspended solids (cellulose fibres and fines) present in the clear filtrate stream.

As the active layer is destroyed, DCM goes easily through the membrane, detecting higher CD and DCOD values in the permeate. The TSS and ash content during NP is higher than in LWC production, so the mentioned erosion is more accused in the first process. As the operating time increases, the membranes pass more time in contact with water so, again, this damage is more marked at higher operation times. This damage on active layer also explains the great variability on the removal efficiencies of CD and DCOD shown in Table 4, as the intermediate and support layers have pore sizes of bigger size.



(a)



(b)

Fig. 6. Electronic microscope photographs of:
(a) fresh membrane; (b) used membrane.

5. CONCLUSIONS

The UF unit presented higher removal efficiencies than the DAF unit for parameters such as ash, turbidity, CD, DCOD and microstickies in all productions studied, independently of inlet water contamination load. DAF unit did not affect CD and

DCOD, while UF reduced CD a 10% (NP) 80% (LWC) and DOCD a 20% (NP) 60% (LWC), respectively.

The UF was more sensitive to the operation time than the DAF, which kept nearly the same removal efficiencies after 312 h of running. As the operation time increased, the UF gave worse removal efficiencies for dissolved fraction than for the colloidal fraction. The cause of this phenomenon was the erosion of the active layer produced by the suspended solids present in the clear filtrate stream. Therefore more resistant membranes need to be used for this application.

The variability of UF removal efficiencies depended of the measured parameter; the system had a high efficiency reproducibility for consistency, ash and turbidity (around 1%), but parameters as TCOD, hardness or sulphates gave efficiency deviations up to 50%, which is related to the specific quality of the raw materials. Further studies will be carried out since this variability may affect key effluent parameters as in the case of the sulphates limit in the Community of Madrid.

The autopsy of the membranes shows that the active layer is destroyed due to the abrasive effect of the suspended solids (cellulose fibres and fines) present in the streams and to the contact with water at higher operation times. For these reasons, DCM goes easily through the membrane, obtaining higher CD and DCOD values in the permeate.

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